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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Sung-Cheol Yoon, et al.)
Serial No.: 10/502,185) Group Art Unit: 1713
Filed: July 21, 2004)
For: METHOD FOR POLYMERIZING)
CYCLOOLEFIN POLYMER)
CONTAINING POLAR FUNCTIONAL)
GROUPS AND ELECTRONIC)
DEVICES EMPLOYING THE)
POLYMERIZED CYCLOOLEFINS)

DECLARATION UNDER 37 CFR § 1.132

Commissioner for Patents
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Heon Kim declares and says that:

1. I am an inventor of the above-referenced U.S. Patent Application serial number 10/502,185, assigned to LG Chem Corporation, and herein referred to as the Application.
2. I graduated from Kyung Hee University with a Master's degree in Chemistry in August 31, 1997.
3. Since November 20, 2000, I have been employed by LG Chem Corporation and have been engaged in the research and development of cycloolefin polymers based on

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Table 1. Results: polymerization of BENB with different exo/endo ratios at 90°C^a

Example	BENB monomer Isomer ratio	Solvent/ monomer ratio	reaction temp.	Mw	Mn	PDI	yield
	(exo/endo)	(w/w)		(g/mol)	(g/mol)		
A ^b	55/45	1/1	90 °C	177,000	92,700	1.91	56%
B ^b	30/70	1/1	90 °C	208,000	124,000	1.68	35%

^a catalyst: Pd(acetate)₂ Palladium acetate], ligand:PCy₃ [tricyclohexyl phosphine]

anion: N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate

^b Polymerizing condition: solvent – toluene; ratio of solvent:monomer 1:1 (w/w) (10.8 g toluene:10.8 g BENB); monomer:Pd molar ratio = 5,000:1; polymerization temperature - 90°C; polymerization time: 18 hrs.

8. As summarized in Table 1, a representative polar norbornene ester monomer, 5-norbornene-2-carboxylic acid butyl ester, abbreviated 'BENB', was polymerized according to the reaction conditions disclosed in the Specification as filed on p. 37, in Example 18 of the instant Specification, with the following differences:

- The exo/endo molar ratio of the BENB monomers and the amount of the solvent to the monomers differs from those used in Example 18 of the present invention, and are 55:45 for Example A, and 30:70 in Example B as shown in Table 1;
- The catalyst used in Ex. A and Ex B shown in Table 1 was palladium acetate, also referred to herein as "Pd(acetate)₂";
- The ligand used is tricyclohexyl phosphine, also referred to herein as "PCy₃";
- The cocatalyst, also referred to herein as the "anion", was N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, also referred to as "dimethylanilinium tetrakis(pentafluorophenyl)borate", and abbreviated (PhNMe₂H)B(C₆F₅)₄;
- As in the conditions described in Example 18 of the Specification, the molar ratio

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of monomer to catalyst is about 5000:1, and the molar ratio of catalyst to anion is 1:2;

- As used herein, the amount of BENB monomer is 10.8 g, and the amount of toluene solvent used is 10.8 g;

- And, as disclosed herein, the polymerization time, also referred to herein as the “reaction time”, was 18 hours.

9. In Table 1 therefore, the difference between Example A and Example B are that the BENB monomer in Example A has an exo isomer content of greater than 50 mol%, and the BENB monomer in Example B has an exo isomer content of less than 50 mol%.

10. In the results shown in Table 1, the following results are seen:

- In Example A in which BENB monomer with an exo/endo molar ratio of 55/45 was used, a cycloolefin polymer was produced with a weight averaged molecular weight (hereinafter Mw) of 177,000, a number averaged molecular weight (hereinafter Mn) of 92,000, a polydispersity (hereinafter PDI) of 1.91, and in a yield of 56% based on the total monomer weight; and

- In Example B in which BENB monomer with an exo/endo molar ratio of 30/70 was used, a cycloolefin polymer was produced with a weight averaged molecular weight (hereinafter Mw) of 208,000, a number averaged molecular weight (hereinafter Mn) of 124,000, a polydispersity (hereinafter PDI) of 1.68, and in a yield of 35% based on the total monomer weight.

11. It is therefore shown in Table 1 that the yield of the exo-rich BENB cycloolefin polymer (Example A), prepared using the catalyst mixture (which is defined as the LGC-R-02-0200-US
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combination of catalyst, ligand, and cocatalyst) exceeds 50% as claimed in claim 1 of the instant claims (see Table 1, Example A); and the yield of the exo-poor BENB (i.e., endo-rich BENB) cycloolefin polymer (Example B), prepared using the catalyst mixture (which is defined as the combination of catalyst, ligand, and cocatalyst) does not exceed 50%, which is a result consistent with the invention as claimed in claim 1 of the instant claims (see Table 1, Example B).

12. Therefore, based on a comparison of Examples A and B of Table 1, we conclude that a cycloolefin polymer, prepared using the catalyst mixture claimed in Claim 1, does not have a yield that exceeds 50% based on the total weight of monomer when using a polar norbornene ester monomer with low exo isomer content of less than 50 mol%.

13. Further experiments were conducted by the Inventors of the present invention to determine the polymerization yield for an exemplary polar norbornene ester monomer at a polymerization temperature of 100°C, under the following conditions and with the following results as shown in Table 2:

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Table 2. Results: polymerization of BENB with different exo/endo ratios at 100°C^c

Example	BENB monomer exo/endo ratio	Solvent/monomer ratio	reaction temp.	Mw	Mn	PDI	yield
	(exo/endo)	(w/w)		(g/mol)	(g/mol)		
C ^d	55/45	1/1	100 °C	157,000	77,900	2.02	67%
D ^d	30/70	1/1	100 °C	150,100	69,900	2.15	45%
E ^e	30/70	2/1	100 °C	102,800	48,300	2.13	26%

^c catalyst: Pd(acetate)₂[Palladium acetate], ligand:PCy₃ [tricyclohexyl phosphine]

anion: N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate

^d Polymerizing condition: solvent – toluene; ratio of solvent:monomer: 1:1 (w/w) (10.8 g toluene:10.8 g BENB); monomer:Pd molar ratio = 5,000:1; polymerization temperature - 100°C; polymerization time: 18 hrs.

^e Polymerizing condition: solvent – toluene; ratio of solvent:monomer: 2:1(w/w) (21.6 g toluene:10.8 g BENB); monomer:Pd molar ratio = 5,000:1; polymerization temperature - 100°C; polymerization time: 18 hrs.

14. As summarized in Table 2, a representative polar norbornene ester monomer, 5-norbornene-2-carboxylic acid butyl ester, abbreviated 'BENB', was polymerized according to the reaction conditions disclosed in the Specification as filed on p. 37, in Example 19 of the instant Specification, with the following differences:

- The exo/endo molar ratio of the BENB monomers and the amount of the solvent to the monomers differs from those used in Example 18 of the present invention, and are 55:45 for Example C, and 30:70 in Examples D and E as shown in Table 2;

- The catalyst used in Examples C, D, and E shown in Table 2 was palladium acetate;

- The ligand used is tricyclohexyl phosphine;

- The anion was dimethylanilinium tetrakis(pentafluorophenyl)borate;

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- As in the conditions described in Example 19 of the Specification, the molar ratio of monomer to catalyst is about 5000:1, and the molar ratio of catalyst to anion is 1:2;

- As used herein, the amount of BENB monomer was 10.8 g for Examples C and D, and the amount of BENB is 10.8 g for Example E; and the amount of toluene solvent used was 21.6g;

- And, as disclosed herein, the polymerization time was 18 hours.

15. In Table 2 therefore, the difference between Example C, and Examples D and E, are that the BENB monomer in Example C has an exo isomer content of greater than 50 mol%, and the BENB monomer in Examples C and D have an exo isomer content of less than 50 mol%.

16. In the results shown in Table 2, the following results are seen:

- In Example C in which BENB monomer with an exo/endo molar ratio of 55/45 and a solvent/monomer ratio of 1:1 was used, a cycloolefin polymer was produced with an Mw of 157,000, an Mn of 77,900, a PDI of 2.02, and in a yield of 67% based on the total monomer weight;

- In Example D in which BENB monomer with an exo/endo molar ratio of 30/70 and a solvent/monomer ratio of 1:1 was used, a cycloolefin polymer was produced with an Mw of 150,100, an Mn of 69,900, a PDI of 2.15, and in a yield of 45% based on the total monomer weight; and

- In Example E in which BENB monomer with an exo/endo molar ratio of 30/70 and a solvent/monomer ratio of 2:1 was used, a cycloolefin polymer was produced with an

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Mw of 102,800, an Mn of 48,300, a PDI of 2.13, and in a yield of 26% based on the total monomer weight.

18. Therefore, based on the above comparison of Examples C, D, and E of Table 2, we conclude that a cycloolefin polymer, prepared using the catalyst mixture claimed in Claim 1 of the instant Application, does not have a yield that exceeds 50% based on the total weight of monomer when using a polar norbornene ester monomer with low exo isomer content of less than 50 mol%.

19. Further experiments were conducted by the Inventors of the present invention to determine the polymerization yield for an exemplary polar norbornene ester monomer at a polymerization temperature of 100°C, under the following conditions and with the following results as shown in Table 3:

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Table 3. Polymerization of high exo BENB (exo/endo=55/45) according to an exemplary method of the '650 patent.

Example	catalyst	Ligand	Anion	Mw	Mn	PDI	Yield ⁱ
F	Pd(acetate) ₂	PCy ₃	LiB(C ₆ F ₅) ₄ 2.5Et ₂ O ^g	27,200	17,300	1.58	> 1%
G	Pd(acac) ₂ ^f	PCy ₃	LiB(C ₆ F ₅) ₄ 2.5Et ₂ O	-	-	-	No reaction
H	Pd(acetate) ₂	PCy ₃	(PhNMe ₂ H) B(C ₆ F ₅) ₄ ^h	261,800	145,100	1.80	72%

^f Pd(acetylacetonate)₂.

^g Lithium tetrakis(pentafluorophenyl)borate·2.5Et₂O.

^h N,N-Dimethylanilinium tetrakis(pentafluorophenyl)borate

ⁱ Polymerizing conditions: solvent – toluene; ratio of solvent:monomer - ca. 1:2 (w/w) (5 g toluene:10.8 g BENB); monomer: Pd molar ratio = 5,000:1; polymerization temperature: 90°C; polymerization time: 18 hrs

20. As summarized in Table 3, a comparison of polymerization of representative polar norbornene ester monomer having a high exo-isomer content (BENB, with a 55/45 exo/endo isomer molar ratio), was run according to the conditions disclosed on p. 37, in Example 18 of the instant Specification, with the following differences:

- In Example F, the catalyst is palladium acetate, and the anion is lithium tetrakis(pentafluorophenyl)borate etherate as disclosed in Example 286 (which is a typographical error and should be Example 296) of the '650 patent, which is the cited reference as disclosed hereinabove;

- In Example G, the catalyst is palladium acetylacetonate (Pd(acac)₂), and the anion is lithium tetrakis(pentafluorophenyl)borate etherate as disclosed in Examples 288 and 297 of the '650 patent;

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-In Example H, the catalyst is palladium acetate, and the anion is dimethylanilinium tetrakis(pentafluorophenyl)borate

- The ligand used in each example is tricyclohexyl phosphine (PCy₃ in Table 3);
- The anion in Examples F and G was lithium tetrakis(pentafluorophenyl)borate etherate, abbreviated as LiB(C₆F₅)₄·2.5Et₂O, and the anion in Example H was dimethylanilinium tetrakis(pentafluorophenyl)borate;

- As in the conditions described in Example 19 of the Specification, the molar ratio of monomer to catalyst is about 5000:1, and the molar ratio of catalyst to anion is 1:2;

- As used herein, the amount of BENB monomer was 10.8 g, and the amount of toluene was 5 g for each of Examples F, G, and H;

- And, as disclosed herein, the polymerization temperature was 90°C, and the polymerization time was 18 hours.

21. In Table 3 therefore, the difference between Examples F and G, and Example H, are that the anion in both Examples F and G are the lithium salt, and the anion in Example H is the dimethylanilinium salt, and Examples F and H use the palladium acetate catalyst and Example G uses palladium acetylacetonate; and where each of Examples F, G, and H have an exo isomer content of greater than 50 mol%.

22. In the results shown in Table 3, the following results are seen:

- In Example F in which palladium acetate catalyst and lithium tetrakis(pentafluorophenyl)borate etherate anion was used according to the '650 patent, a cycloolefin polymer was produced with an Mw of 27,200, an Mn of 17,300, a PDI of 1.58,

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and a very low yield of less than 1% based on the total monomer weight;

- In Example G in which palladium acetylacetonate catalyst and lithium tetrakis(pentafluorophenyl)borate etherate anion was used according to the '650 patent, no cycloolefin polymer was produced; and

- In Example H in which palladium acetate catalyst and dimethylanilinium tetrakis(pentafluorophenyl)borate etherate anion was used according to the present invention, a cycloolefin polymer was produced with an Mw of 261,800, an Mn of 145,100, a PDI of 1.80, and a yield of 72% based on the total monomer weight.

23. It is therefore shown in Table 3 that the yield of the exo-rich BENB cycloolefin polymer (Example H), prepared using the claimed catalyst mixture, exceeds 50% as claimed in claim 1 of the instant claims (see Table 3, Example H); and the yield of the exo-rich BENB cycloolefin polymerization reactions using catalyst compositions as disclosed in the '650 patent (Examples F and G) does not exceed 50%, where the highest yield of these two Examples is achieved by Example F with a yield of less than 1%.

24. Based on the above comparison of Examples F, G, and H of Table 3, we conclude that a cycloolefin polymer, prepared using the catalyst composition disclosed in the cited reference (the '650 patent), cannot be prepared in a yield that exceeds or even approaches 50% based on the total weight of monomer even when using a polar norbornene ester monomer with a high exo-isomer content (BENB 55/45 exo/endo molar ratio) in conjunction with exemplary catalysts disclosed in Examples 286[sic], 288, and 297 of the '650 patent as seen in Examples F and G; whereas, a cycloolefin polymer can be prepared

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in high yield of greater than 50% (specifically, 72% in Example H) when using the particular catalyst mixture selected according to the method claimed in Claim 1 of the instant claims, with a polar norbornene ester monomer with exo isomer content of greater than 50 mol%.

25. Therefore also, we further conclude that the selection of catalyst and anion, and the specific combinations of these, are of great significance in achieving conversion of high exo norbornene ester monomers, and that a particular combination of catalyst, ligand, and anion that can function to provide the desired yield is not disclosed by the reference (the '650 patent).

26. Further experiments were conducted by the Inventors of the present invention to compare the properties of polymer films prepared from cycloolefin polymers containing different ratios of exo and endo isomers of norbornene monomers having polar groups.

27. Polymer films were prepared from two different 20 wt% polymer solutions, in which a high-exo content polymer solution was prepared by dissolving the cycloolefin polymer of Example C, prepared using a high-exo norbornene monomer (BENB, exo/endo ratio = 55/45), and a high-endo (i.e., low-exo) content polymer solution was prepared by dissolving the cycloolefin polymer of Example E, prepared using a high-endo cycloolefin polymer (BENB, exo/endo ratio = 30/70). Each polymer solution was prepared by dissolving the polymer in methylene chloride.

28. The polymer solutions were each cast on a separate glass plate and dried to prepare polymer films, which are shown in the EXHIBIT. As seen in the EXHIBIT, the polymer

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film prepared from the high-endo cycloolefin polymer of Example E (EXHIBIT, right-hand photograph) broke into pieces when it was separated from the glass plate. In contrast, the polymer film prepared from the high-exo polymer (exo/endo ratio = 55/45, Example C) was cleanly separated from the glass plate without defects (EXHIBIT, left-hand photograph).

29. This difference in separability of the two polymer films from their respective substrates is evidence offered by the Inventors hereof to demonstrate that the high-endo polymer film prepared from Example E has a brittleness higher than that of the high-exo polymer film, and hence the mechanical properties of the high-endo polymer film are inferior relative to the mechanical properties high-exo polymer film.

30. Thus, it can be concluded that the polymer film prepared from a cycloolefin polymer prepared from the method claimed in Claim 1 from norbornene monomers having an exo isomer content of more than 50 mol%, has superior mechanical properties relative to a polymer film prepared from a comparable polymer prepared from a norbornene monomer having polar groups but with a low molar percentage of exo isomer for the norbornene monomer having polar groups.

31. I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the

United States Code and that such willful false statements may jeopardize the validity of the
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patent.

Heon

Heon Kim

Date: October 17, 2007

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